

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

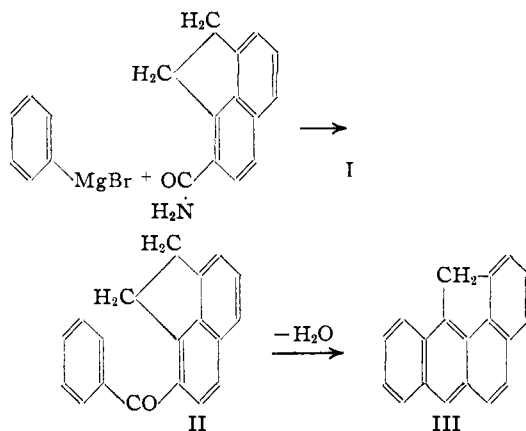
Synthesis of 1',9-Methylene-1,2-benzanthracene and Related Hydrocarbons

BY LOUIS F. FIESER AND JAMES CASON¹

It seemed of interest for a number of reasons to synthesize 1',9-methylene-1,2-benzanthracene (III) and investigate its chemical properties and possible biological actions. Like the as yet unknown² 1',9-dimethyl compound, the hydrocarbon may constitute a simplified model of the highly reactive and powerfully carcinogenic 3,4-benzpyrene, and the presence of a methylene group at the meso position 9 may confer upon the substance some of the special properties of the cholanthrenes³ or of 8,9-dimethylene-1,2-benzanthracene.⁴ It is also interesting to learn whether the 1',9-methylene derivative, considered as a simple alkylated 1,2-benzanthracene, is associated in biological properties with the moderately carcinogenic³ 9-methyl compound⁵ or with the inactive³ 1'-methyl derivative.^{2,6} While 1',9-methylene-1,2,5,6-dibenzanthracene⁷ gives a moderate yield of tumors in mice only after a very extended induction period,³ the relationship between the inactive 9,10-dimethyl-1,2,5,6-dibenzanthracene⁸ and the highly potent 9,10-dimethyl-1,2-benzanthracene⁹ suggests that the simpler 1',9-methylene compound is well worthy of investigation.

One possible route to the desired hydrocarbon involved the synthesis and pyrolysis of 1-benzoylacenaphthene (II). A small quantity of this ketone was obtained in preliminary work by M. E. Gross from 3-acenaphthylmagnesium iodide and benzonitrile, but this route was temporarily abandoned because of the difficulty of obtaining adequate quantities of the required 3-iodoacenaphthene from the rather inaccessible 3-nitro compound (literature, ref. 7). The situation is considerably altered, however, by the recent observation that 3-acetoacenaphthene can be prepared very easily by the acetylation of the hydrocarbon in the presence of anhydrous hydrogen fluoride.¹⁰

In a large-scale preparation the yield of satisfactory 3-isomer was 29%, and the hypohalite oxidation to 3-acenaphthoic acid proceeded very smoothly. In one trial the Friedel and Crafts condensation of the acid chloride with benzene took an abnormal course and gave a sparingly soluble yellow product. The amide (I), obtainable from the acid with little loss, condensed very smoothly if slowly with phenylmagnesium bromide, giving 1-benzoylacenaphthene (II) in 95% yield. On pyrolysis the ketone suffered loss of water at 425° and

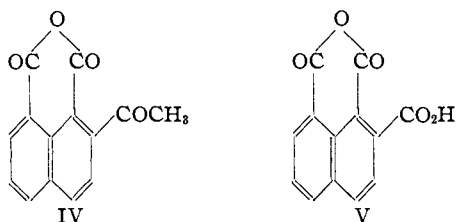


1',9-methylene-1,2-benzanthracene (III) was isolated in a satisfactory condition in 13% yield. The Elbs reaction proceeds about as expected, the difficulty of ring closure into a benzenoid nucleus being offset by the favorable utilization of a methylene group of an alicyclic ring. The hydrocarbon (m. p. 123°) has a faint greenish-yellow color which was retained on purification through the picrate, by chromatographic adsorption, and treatment with maleic anhydride. Like methylcholanthrene and 3,4-benzpyrene, and in contrast to 1',9-methylene-1,2,5,6-dibenzanthracene, it couples rapidly (deep color in five minutes) with *p*-nitrobenzenediazonium chloride in acetic acid solution.¹¹ The hydrocarbon is attacked rather readily by lead tetraacetate and apparently is converted into a mixture of products. The condensation with methylformanilide was tried with unpromising results, for at 0° a part of the material was recovered unchanged and a part converted into tars.

- (1) Research Fellow on funds from the National Cancer Institute.
- (2) Fieser and Seligman, *THIS JOURNAL*, **60**, 170 (1938).
- (3) Review paper: Fieser, *Am. J. Cancer*, **34**, 37 (1938).
- (4) Fieser and Seligman, *THIS JOURNAL*, **57**, 2174 (1935).
- (5) Newman, *ibid.*, **59**, 1003 (1937); Cook, Robinson and Goulder, *J. Chem. Soc.*, 393 (1937).
- (6) Cook and Robinson, *ibid.*, 505 (1938).
- (7) Fieser and Hershberg, *THIS JOURNAL*, **57**, 1681 (1935).
- (8) Cook, *J. Chem. Soc.*, 489 (1931); Akin and Bogert, *THIS JOURNAL*, **69**, 1564 (1937).
- (9) Bachmann and Chemerda, *ibid.*, **60**, 1023 (1938); Newman, *ibid.*, **60**, 1141 (1938).
- (10) Fieser and Hershberg, *ibid.*, **61**, 1272 (1939).

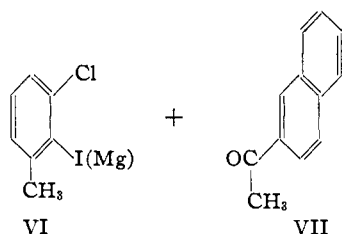
- (11) Fieser and Campbell, *ibid.*, **60**, 1142 (1938).

In preparing the starting material some further study was made of the reaction between acenaphthene and acetic acid in the presence of hydrogen fluoride. The yield and the ratio of isomers was the same when acetyl chloride was used in place of the free acid. It was ascertained also that neither 1- nor 3-acetoacenaphthene suffers rearrangement under the conditions of the acylation. 3-Acetoacenaphthene picrate was found to exist in two polymorphic forms of the same melting point, one separating as orange prisms and the other appearing as yellow needles. 1-Acetoacenaphthene was converted into two new reference compounds of the naphthalene series. Oxidation with sodium dichromate in acetic acid solution gave 2-aceto-1,8-naphthalic anhydride (IV), and



oxidation of 1-acenaphthoic acid by the same method gave 2-carboxy-1,8-naphthalic anhydride (V).

Some further synthetic experiments may be reported. A satisfactory procedure was worked out for the preparation of 2-iodo-3-chlorotoluene (VI) from 2-iodo-3-nitrotoluene and attempts were made to condense the Grignard reagent from the dihalide with β -acetone-naphthalene, in the hope of



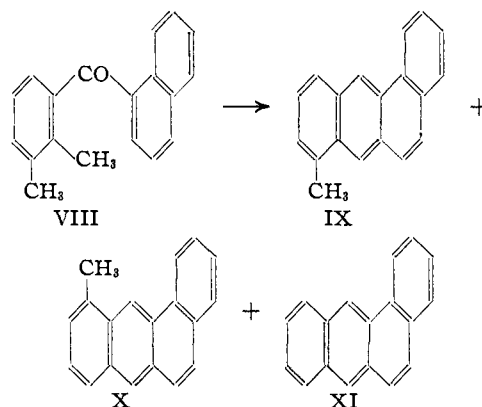
obtaining a ketone which might be convertible into 5,10-dimethyl-1,2-benzanthracene¹² by the synthetic method employed for the 3,9-isomer.¹³ The reaction proceeded very poorly and the small amount of product obtained after dehydration contained considerably less than the expected amount of chlorine and could not be hydrogenated. Condensation with β -naphthonitrile also gave poor results, and the difficulty is thus attributable to the hindered character of the more reactive halogen

(12) Fieser and Newman, *THIS JOURNAL*, **58**, 2376 (1936).

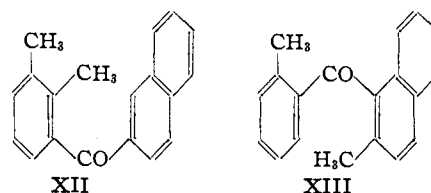
(13) Fieser and Seligman, *ibid.*, **61**, 136 (1939).

substituent, and perhaps to the opportunity for some interaction with the *o*-chloro atom.

As a possible route to the known 5-methyl-1,2-benzanthracene,^{12,14,15,16} *vic.-o*-xylyl α -naphthyl ketone (VIII) was synthesized from *vic.-o*-xylylene and α -naphthylmagnesium bromide and submitted to pyrolysis at 425–430°. There was



obtained a mixture of hydrocarbons found to contain the 5-methyl compound IX, the 8-methyl isomer¹⁷ X, and 1,2-benzanthracene (XI). The formation of 8-methyl-1,2-benzanthracene evidently is the result of a rearrangement, presumably involving the migration of the xylyl group of the ketone VIII from the α - to the β -position in the naphthalene nucleus, as postulated for the formation of 1,2,5,6-dibenzanthracene on pyrolysis of 1-(α -naphthoyl)-2-methylnaphthalene.¹⁸ The isomeric *vic.-o*-xylyl β -naphthyl ketone (XII) was prepared for comparison and pyrolyzed.



The hydrocarbon mixture resulting in fairly good yield was found to consist in large part of 8-methyl-1,2-benzanthracene, identified as the quinone, and no 1,2-benzanthracene was noted. Because of the difficulty of isolating a pure product from the mixture, this is not a practical preparative method. The observation that a methyl group is in part retained at position 8 is of interest because of the contrasting result obtained by

(14) Cook, *J. Chem. Soc.*, 1591 (1932).

(15) Bachmann and Wilds, *THIS JOURNAL*, **60**, 624 (1938).

(16) Fieser and Johnson, *ibid.*, **61**, 1647 (1939).

(17) (a) Fieser and Johnson, *ibid.*, **61**, 168 (1939); (b) Cook and Iball, *J. Chem. Soc.*, 270 (1939).

(18) Cook, *ibid.*, 487 (1931).

Cook¹⁸ on pyrolysis of 1-*o*-toluyl-2-methylnaphthalene (XIII). With this ketone, where ring closure involved condensation into a benzenoid nucleus, the sole product was 1,2-benzanthracene. With the isomer XII, in which the more reactive naphthalene nucleus is involved in the cyclization, the pyrolysis proceeds more smoothly, for the second methyl group is largely retained. This is in line with the high yield of 1,2-benzanthracene from *o*-tolyl β -naphthyl ketone,¹⁹ in contrast to the low yield from the isomeric 1-benzoyl-2-methylnaphthalene.²⁰ The observation that methyl groups in the α -positions 5 and 8 of the benzanthracene system withstand to some extent the drastic conditions of the Elbs reaction substantiates previous comments²¹ on the subject.

Experimental Part²²

1-Acetoacenaphthene was prepared as described¹⁰ from 154 g. of powdered acenaphthene, 65 g. of acetic acid, and 750 g. of anhydrous hydrogen fluoride, allowed to stand in a copper flask for forty-eight hours with occasional stirring. After adding soda solution and benzene, filtering, separating the green benzene layer and distilling, there was obtained 182 g. of total ketone, b. p. 193–195° at 8 mm. Successive crystallizations of the top fraction from 400 cc., 500 cc., and 650 cc. of methanol gave 53 g. of the 1-isomer, m. p. 104–105°, and 4.5 g. more of the pure material was obtained from the final mother liquor: yield 29%.

When acetyl chloride (added slowly) was used in place of acetic acid neither the total yield nor the ratio of isomers was affected. To test the stability of the ketone under the conditions of the acylation, 5 g. of 1-acetoacenaphthene was treated with 200 g. of anhydrous hydrogen fluoride and the solution allowed to stand for forty-two hours. The recovered and distilled product on crystallization from methanol gave 4 g. of starting material, m. p. 104.5–105°, and 0.6 g. of the corresponding picrate, m. p. 114–114.5°, was obtained from the mother liquor.

The picrate crystallized from methanol as light yellow needles, m. p. 114.5–115°.

Anal. Calcd. for C₂₀H₁₆O₈N₃: N, 9.88. Found: N, 9.97.

The trinitrobenzene derivative, which is considerably less soluble, formed bright yellow plates from alcohol, m. p. 113.5–114°.

Anal. Calcd. for C₂₀H₁₅O₇N₃: N, 10.27. Found: N, 10.12.

3-Acetoacenaphthene was separated as the picrate from the mother liquors from the first two crystallizations of the 1-isomer. After several crystallizations from methanol a total of 39 g. of satisfactory product, m. p. 97–

97.5°, was collected. Treated with ammonia, this afforded 16 g. of 3-acetoacenaphthene, m. p. 69–69.5°; after melting and freezing several times the polymorphic form, m. p. 56.5–57.5°, was obtained. The 3-ketone (5 g.) was recovered unchanged (4 g., m. p. 69.2–69.6°) after standing for forty-two hours in hydrogen fluoride solution.

The picrate was found to exist both in the orange-prism form previously described¹⁰ and in the form of long, fine, yellow needles of the same m. p. If the yellow modification is introduced to a bath preheated to 93° it melts at once, but when heated gradually the m. p. is 97–97.5°. The orange picrate separates as cubic or elongated prisms when crystallization occurs at or above room temperature, while the yellow picrate crystallizes from a colder, more dilute solution. The transition temperature seems to be about 20–25°. If the temperature is lowered after the orange form has started to separate, yellow needles are deposited from the same solution. The picrates are interconvertible and yield the same ketone.

Anal. (yellow picrate). Calcd. for C₂₀H₁₆O₈N₃: N, 9.88. Found: N, 9.75.

2-Aceto-1,8-naphthalic Anhydride (IV).—A mixture of 1 g. of 1-acetoacenaphthene and 8 g. of sodium dichromate in 20 cc. of acetic acid was heated at 55–65° for one hour, boiled for three minutes, and poured (cold) into 100 cc. of water. The tan precipitate was crystallized twice from acetic acid containing a few drops of acetic anhydride (Norite), giving 90 mg. of almost colorless, diamond-shaped plates of the constant m. p. 219–219.3°.

Anal. Calcd. for C₁₄H₈O₄: C, 70.00; H, 3.38. Found: C, 69.86; H, 3.54.

1-Acenaphthoic Acid.¹⁰—A stirred solution of 15 g. of 1-acetoacenaphthene in 300 cc. of dioxane (purified with sodium) was treated in the course of twenty minutes with a hypochlorite solution²³ from 48 g. of HTH, 34 g. of potassium carbonate, 9.6 g. of potassium hydroxide, and 300 cc. of water. After an initial exothermic reaction (to 75°), the temperature was maintained at 60° with stirring for one-half hour (one hour for a 50-g. run). Excess reagent was destroyed with bisulfite, the solution was cooled, diluted with 1 l. of water, filtered from a slight sediment, and acidified. The precipitate was coagulated by boiling, collected and washed; yield, 14.5 g. (95.5%), m. p. 254–256°. No further purification is required for the following reactions.

2-Carboxy-1,8-naphthalic Anhydride (V).—To a solution of 1 g. of 1-acenaphthoic acid in 30 cc. of acetic acid at 90°, 6 g. of sodium dichromate was added gradually at such a rate as to maintain a temperature of 90–95°. After forty minutes at this temperature and boiling for five minutes the solution was poured into 100 cc. of water containing 10 cc. of concentrated hydrochloric acid. After boiling for a few minutes and cooling, the product slowly separated as light yellow crystals (260 mg.). Two crystallizations from acetic acid containing a little acetic anhydride gave colorless plates melting constantly at 297.5–298.5°.

Anal. Calcd. for C₁₃H₆O₅: C, 64.46; H, 2.48. Found: C, 64.48; H, 2.65.

The methyl ester, prepared with diazomethane in ether

(23) Newman and Holmes, *Org. Syntheses*, **17**, 65 (1937).

(19) Bachmann, *J. Org. Chem.*, **1**, 347 (1938); Fieser and Hershberg, *This Journal*, **59**, 2502 (1937).

(20) Fieser and Dietz, *Ber.*, **62**, 1827 (1929).

(21) Fieser and Peters, *This Journal*, **54**, 3742 (1932).

(22) All melting points are corrected. Microanalyses by Lyon Southworth.

suspension, crystallized from acetic acid-anhydride as small, nearly colorless plates, m. p. 191–192°.

Anal. Calcd. for $C_{14}H_{10}O_5$: C, 65.63; H, 3.15. Found: C, 65.80; H, 3.29.

1-Acenaphthoyl Chloride.—The precipitated acid (1 g.) was refluxed with purified thionyl chloride (2 cc.) for two hours, the excess reagent evaporated at reduced pressure, and the solidified residue crystallized from benzene-ligroin (Norite). This gave tan needles, m. p. 109.5–110.5°; yield 0.85 g. (82%). A recrystallized sample melted at 110–111°.

Anal. Calcd. for $C_{13}H_9OCl$: C, 72.02; H, 4.20. Found: C, 71.85; H, 4.40.

When a good grade of commercial thionyl chloride was used without purification with quinoline and linseed oil, both the acid chloride and the amide obtained from it contained impurities which persisted after numerous crystallizations.

On treatment of the acid chloride (3.8 g.) in benzene (30 cc.) with aluminum chloride (2.9 g.) at the refluxing temperature there was obtained a yellow substance which is not altered by prolonged boiling with dilute acid, is sparingly soluble in organic solvents, decomposes above 200°, and leaves an ash on ignition.

1-Acenaphthamide.—The crude acid chloride from 12 g. of 1-acenaphthoic acid was dissolved in 150 cc. of warm dioxane and the solution was added rapidly to 120 cc. of well-stirred, cold, concentrated aqueous ammonia solution. After thirty minutes 500 cc. of water was added, and after stirring for fifteen minutes longer the precipitated amide was collected. The yield of light tan powder melting at 219–222° and suitable for the Grignard reaction was 12 g. (quantitative). A sample recrystallized from alcohol formed colorless, short needles, m. p. 227–228° (constant).

Anal. Calcd. for $C_{13}H_{11}ON$: N, 7.11. Found: N, 6.96.

1-Benzoylacenaphthene.—Ten grams of the solid, precipitated amide was added to the Grignard reagent from 5.1 g. of magnesium and 32 g. of bromobenzene in 200 cc. of ether and the mixture was refluxed with stirring for seventy-two hours. The complex, which separated as a solid, was decomposed with ice (50 g.) and concentrated hydrochloric acid (25 cc.), giving the ketimine hydrochloride as a light yellow solid insoluble in either the water or ether layer. The ether was evaporated and after adding 35 cc. each of concentrated hydrochloric acid, glacial acetic acid and toluene the mixture was refluxed two hours for hydrolysis. The toluene layer was separated, washed with water and bicarbonate solution, dried and distilled. The ketone distilled as a light yellow oil, b. p. 210–215° at 1 mm., which crystallized at once on cooling. The yield of distilled material suitable for pyrolysis was 12.4 g. (95%). A sample crystallized for analysis from methanol formed colorless needles, m. p. 91.5–92°.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 88.34; H, 5.46. Found: C, 88.02; H, 5.48.

The ketone was also prepared by M. E. Gross starting with 1-nitroacenaphthene (19.8% yield in the nitration), through the amine (88%) and iodide (yield about 45%,

in two experiments the material completely decomposed on vacuum distillation). The condensation of benzonitrile with the lithium derivative was tried without success; with the Grignard reagent the yield of distilled ketone was 15%. A purified sample melted at 93–94°, uncorr. (found: C, 88.23; H, 5.32).

1',9-Methylene-1,2-benzanthracene.—A 9.9-g. charge of distilled 1-benzoylacenaphthene was heated in a bath at 420–425° for forty minutes and the hydrocarbon distilled at 1 mm. and a bath temperature of 250–350°. The solidified distillate was dissolved in 100 cc. of alcohol, 3.5 g. of picric acid was added, and after concentrating to a volume of about 50 cc. there separated on slow cooling 2.75 g. of dark red picrate. A solution of this in 40 cc. of benzene was put through a tower of alumina and the hydrocarbon, which showed a bright blue fluorescence in ultraviolet light, was washed through until a lighter blue fluorescent zone reached the bottom of the tower. The benzene was evaporated and the hydrocarbon was crystallized from 50 cc. of alcohol, giving light yellow plates, m. p. 121.5–122°; yield, 1.2 g. (12.9%). After three further crystallizations the hydrocarbon (0.85 g.) melted at 122.5–123°; a sample which had been crystallized repeatedly as the trinitrobenzene derivative melted at 122.7–123.1°. The purified material (plates) has a faint fluorescent greenish-yellow color not removed by purification as above, crystallization of the picrate, chromatographic adsorption, or treatment with maleic anhydride.

Anal. Calcd. for $C_{19}H_{12}$: C, 94.96; H, 5.04. Found: C, 94.92; H, 5.08.

The picrate crystallizes from alcohol in the presence of excess picric acid as dark red needles, m. p. 141.5–142°.

Anal. Calcd. for $C_{25}H_{15}O_7N_3$: N, 8.95. Found: N, 8.51.

The trinitrobenzene derivative separates from alcohol in bright orange needles, m. p. 162.5–163°.

Anal. Calcd. for $C_{25}H_{15}O_6N_3$: N, 9.27. Found: N, 9.21.

2-Iodo-3-chlorotoluene.—2-Iodo-*m*-toluidine was prepared by the hydrogenation of 2-iodo-3-nitrotoluene (30 g.) in acetic acid (100 cc.) in the presence of Adams catalyst (0.3 g.), absorption being complete in ten hours. The filtered solution was treated with 20 cc. of 12 *N* sulfuric acid and 1 l. of ether and the precipitated salt collected (35.5 g., 94%). For conversion to the amine this salt was dissolved by warming in 400 cc. of water containing 4 cc. of 12 *N* sulfuric acid, the solution was filtered from a little dark material (colorless filtrate), and neutralized carefully at 0° with cold ammonium hydroxide. The amine separated in a colorless, crystalline condition, m. p. 40–40.6° (compare 41–42°²⁴); yield 21.7 g. (82% from the nitro compound).

For conversion to the iodochlorotoluene it is best to omit isolation of the amine or its salt. The acetic acid solution from the hydrogenation of 20 g. of the nitro compound was diluted with 290 cc. of water and 58 cc. of concentrated hydrochloric acid and cooled to –5° with stirring. To the resulting suspension of the hydrochloride a cooled solution of 6.3 g. of sodium nitrite in 35 cc. of water was added all at once. After stirring for thirty

(24) Wheeler and Liddle, *Am. Chem. J.*, **42**, 452 (1909).

minutes below 0°, 10 g. of urea was added; after twenty minutes more the cold (unfiltered) solution was added to a stirred solution of 9.1 g. of cuprous chloride in 43 cc. of concentrated hydrochloric acid and 11 cc. of water. The complex began to decompose at once, and a dark oil began to separate. After stirring for one-half hour below 0° and for one hour longer after removal from the cooling bath, the mixture was steam distilled. The heavy oil, which distilled slowly, was extracted with ether, washed with alkali, acid, and water, dried and distilled. This gave a nearly colorless oil, b. p. 123–125° at 14 mm.; yield 14.3 g. (74.5%, from the nitro compound). The product solidified at about 24° and melted at 25.5–26.5°; recrystallized from methanol it formed colorless plates, m. p. 27.3–27.6°.

Anal. Calcd. for C₇H₆Cl₂: C, 33.28; H, 2.38. Found: C, 33.02; H, 2.64.

Long and Dains²⁵ report the preparation of the dihalide as a yellow oil which darkened on standing and solidified at –26°.

The dihalide formed a Grignard reagent readily, but no acid was obtained on attempted carbonation with solid carbon dioxide. From the reaction with β-acetonaphthalene there was obtained after dehydration a small yield (30%) of product which contained only about three-quarters of the expected amount of halogen and which could not be hydrogenated in the presence of Adams catalyst in acetic acid or, at high pressure, using copper chromite or Raney nickel. The reaction with β-naphthonitrile also gave a low yield (30%) of non-homogeneous oil.

vic.-Cyano-o-xylene.—*vic.-o-Xylylidine* was prepared (first experiments by T. G. Webber, Jr.) by reduction of the nitro compound with iron and water according to James, Snell and Weissberger,²⁶ but in better yield (91.5%; b. p. 98–100° at 11 mm., 118–119° at 25 mm.). Catalytic reduction also proceeded smoothly (92%) but was less convenient. The amine (20 g.) in water (140 cc.) and concentrated hydrochloric acid (54 cc.) was diazotized at –5° with sodium nitrite (13.7 g.) in water (85 cc.), the solution was neutralized with solid sodium carbonate, and the dark solution was added to a cold solution prepared from 29 g. of sodium cyanide and 20 g. of cuprous chloride in 130 cc. of water. A dark yellow complex separated and began to decompose on allowing the mixture to come to room temperature. After steam distillation the nitrile was extracted with ether, washed with alkali and water, dried and distilled, giving a colorless oil, b. p. 105–107° at 11 mm.; yield 8.6 g. (40%). Brunner, Hofer and Stein²⁷ obtained about the same yield by a different procedure.

vic.-o-Xylyl α-Naphthyl Ketone (VIII) was prepared by adding 5.5 g. of *vic.-cyano-o-xylene* in 35 cc. of benzene to the reagent from 10.5 g. of α-bromonaphthalene and 1.3 g. of magnesium in 40 cc. of ether and 10 cc. of benzene. After most of the ether had been distilled, the mixture was refluxed with stirring overnight. After adding 40 g. of ice and 20 cc. of concentrated hydrochloric acid and

removing the solvent with steam, 30 cc. more hydrochloric acid was added together with 30 cc. of acetic acid and 40 cc. of toluene. After refluxing for six hours the collected product distilled, after a fore-run containing naphthalene, as a viscous yellow oil, b. p. 190–195° at 1 mm.; yield 9.7 g. (89%). The ketone was not obtained crystalline.

Anal. Calcd. for C₁₉H₁₆O: C, 87.66; H, 6.19. Found: C, 88.24; H, 6.18.

Pyrolysis of VIII.—In one experiment 2.2 g. of *vic.-o-xylyl α-naphthyl ketone* was heated with 0.25 g. of zinc dust at 425–430° for two hours. Distillation at 1 mm. gave 1 g. of crystalline yellow solid, and after a prolonged process of fractionation of the hydrocarbon from alcohol and of its picrate from benzene–hexane there was obtained 10 mg. of **5-methyl-1,2-benzanthracene**, m. p. 154–156°. A mixture with a known sample¹² melted at 156–158°; there was a large depression on admixture with 1,2-benzanthracene.

In another experiment, conducted as above except that no zinc dust was used, there was isolated a small quantity of **1,2-benzanthracene**, m. p. 154–157°, mixed m. p. 155–157°. A picrate fraction (1 g., m. p. 153–154°) which had been crystallized repeatedly from alcohol and then put through an adsorption tower in benzene gave a hydrocarbon mixture melting below 125° and apparently containing 8-methyl-1,2-benzanthracene. Since a pure product could not be isolated, the material was oxidized to the quinone as described by Fieser and Johnson.^{17a} The yellow zone in the tower was eluted with benzene–methanol, and the material was fractionally crystallized from acetone. One fraction was obtained as long, light yellow needles of **8-methyl-1,2-benzanthraquinone**, m. p. 194.5–196°, mixed m. p. 195–196° (sample, ref. 17a). Another small fraction formed fluffy yellow needles, m. p. 171–172.5°, and probably was 5-methyl-1,2-benzanthraquinone.

vic.-o-Xylyl β-naphthyl ketone (XII) was obtained as described for the isomer in 87% yield as a yellow oil which slowly solidified. A sample crystallized several times from methanol formed colorless prisms, m. p. 62–63°.

Anal. Calcd. for C₁₉H₁₆O: C, 87.66; H, 6.19. Found: C, 87.93; H, 6.19.

Pyrolysis of XII.—Pyrolysis of 2.6 g. of the β-naphthyl ketone with 0.5 g. of zinc dust at 420–425° for one and one-half hours gave 1.8 g. of distilled product. No pure hydrocarbon could be isolated by crystallization as the hydrocarbon, picrate, or trinitrobenzene derivative; the best sample of hydrocarbon melted at 110–112°, and a mixture with 8-methyl-1,2-benzanthracene^{17a} melted at 114–116°. A 11-g. sample of hydrocarbon mixture, m. p. 98–108°, was oxidized to the quinone and after adsorption on alumina and crystallization from acetone there was obtained 45 mg. of **8-methyl-1,2-benzanthraquinone**, m. p. 196–196.5° and 130 mg., m. p. 192–195°. This showed no depression with an authentic sample.^{17a} The amount of this quinone was about three-quarters of that obtained from the pure hydrocarbon by Fieser and Johnson.^{17a} The mother liquors contained another quinone which was not isolated in a pure condition but which melted at 162–164° and showed a large depression when mixed with 1,2-benzanthraquinone.

(25) Long and Dains, *Kansas Univ. Science Bull.*, **9**, 208 (1930).

(26) James, Snell and Weissberger, *THIS JOURNAL*, **60**, 2085 (1938).

(27) Brunner, Hofer and Stein, *Monatsh.*, **63**, 92 (1933).

Summary

1-Benzoylacenaphthene, obtained conveniently from the available 1-aceto compound by a phenyl Grignard reaction on the corresponding amide, gives 1',9-methylene-1,2-benzanthracene on pyrolysis in 13% yield.

Further data are given on the preparation of 1-acetoacenaphthene by the hydrogen fluoride procedure and on the characterization and oxidation of the ketone.

A study of the pyrolysis of *vic.-o*-xylyl α - and β -naphthyl ketones shows that methyl groups in the α -positions 5 and 8 of the 1,2-benzanthracene molecule withstand to some extent the conditions of the Elbs reaction but that with the α -naphthyl isomer there appears to be both migration of the aryl group and partial elimination of the methyl substituent.

CONVERSE MEMORIAL LABORATORY

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 3, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Diffusion Velocity and Molecular Weight. I. The Limits of Validity of the Stokes-Einstein Diffusion Equation

BY LEO FRIEDMAN AND PAUL G. CARPENTER¹

Considerable interest has been evidenced in recent years in the use of diffusion velocity studies as a means of determining molecular weights.²⁻⁴ Some results have been obtained that are in excellent agreement with results yielded by other methods.³ On the other hand, the results of Northrop and Anson on hemoglobin^{2,5} have been discouraging, as were the results of one of the authors on gelatin (to be reported in a later paper of this series).

In the use of diffusion velocity as a means of determining molecular weights, too little attention has been paid to the concentration of the diffusate. Since the Stokes-Einstein diffusion equation makes no provision for change in concentration and is derived on the assumption of free diffusion, it would appear that the diffusion coefficient to be used for the calculation of molecular weight should be determined at infinite dilution.

In a classical paper on this subject Sutherland⁶ made an effort to apply the Stokes-Sutherland-Einstein equation to the evaluation from diffusion data of the molecular weights of a number of non-electrolytes ranging in molecular weight from methyl alcohol to raffinose. Undoubtedly his failure to obtain closer agreement between diffu-

sion data and molecular weight was due to inaccuracy of data available at that time. In this paper he also gives a general empirical equation for use as the molecular weight becomes small.

Attempt to Evaluate Molecular Weights of Non-Electrolytes from their Diffusion Coefficients.—Examination of the diffusion data for non-electrolytes to be found in the "International Critical Tables" shows that the diffusion coefficient varies considerably with the concentration of the diffusate. Calculations of the molecular weights of these non-electrolytes have been made by use of the Stokes-Einstein diffusion equation

$$D = \frac{RT}{N} \frac{1}{6\pi\eta r}$$

combined with the relationship

$$M = \frac{4}{3}\pi r^3 d N$$

Results of several of these calculations are given in Table I. In the case of each non-electrolyte, the last value of the diffusion coefficient labeled 0 concentration has been calculated from the molecular weight of the substance. It is to be observed in each case that the value so obtained is not unreasonable when compared with the experimental values reported in the "International Critical Tables."

If the results of Table I are represented graphically by plotting the diffusion coefficient against the square root of the concentration of the diffusate, it is possible to draw a straight line from the theoretically calculated diffusion coefficient through the experimental points taken from the

(1) Present address: Willamette University, Salem, Oregon.

(2) J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

(3) J. W. McBain and T. S. Lau, *THIS JOURNAL*, **53**, 59 (1931).

(4) J. W. McBain, C. R. Dawson and H. A. Barker, *ibid.*, **56**, 1021 (1934).

(5) M. L. Anson and J. H. Northrop, *J. Gen. Physiol.*, **29**, 575 (1937).

(6) W. Sutherland, *Phil. Mag.*, [6] **9**, 781 (1905).